STATUTORY DECLARATION

I, Jun Hee PARK, a citizen of the Republic of Korea and a staff member of Bae, Kim & Lee, specializing in "Semiconductor Devices", do hereby declare that:

1) I am conversant with the English and Korean languages and am a competent translator thereof;

2) To the best of my knowledge and belief, the following is a true and correct translation of the Priority Document (No. KR 1999-54365) in the Korean language already filed with the Korean Industrial Property Office on December 2, 1999.

Signed this 12th day of May, 2003

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THE KOREAN INDUSTRIAL PROPERTY OFFICE

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Applicant: Hyundai Electronics Industries Co., Ltd.

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COMMISSIONER

TITLE OF THE INVENTION

Over-coating Composition for Photoresist, and Processes for Forming Photoresist Patterns Using the Same

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1a shows a pattern profile obtained when the photoresist resin having little absorbance to a light source is used;

Figure 1b shows a pattern profile obtained when the photoresist resin having much absorbance to a light source is used;

Figure 2 shows a photoresist pattern obtained in Comparative Example 1;

Figure 3 shows a photoresist pattern obtained in Comparative Example 2;

Figure 4 shows a photoresist pattern obtained in Comparative Example 3;

Figure 5 shows a photoresist pattern obtained in Comparative Example 5; and

Figure 6 shows a photoresist pattern obtained in Invention Example 3.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a novel over-coating composition. In particular, the present invention relates to an over-coating composition comprising a basic compound, which is particularly suitable in a photolithography process using photoresist resins having a low light transmittance thereby obtaining vertical pattern not slope pattern.

2. Description of the Background Art

Fine photoresist patterns of 150 nm L/S have successfully been developed

using a light source which produces light having wavelength of 248nm (KrF). Attempts at forming high quality fine circuit patterns smaller than 150 nm have thus far been relatively unsuccessful. These attempts have used light sources which generate short wavelengths such as ArF (193nm), F_2 (157nm) and EUV (Extremely Ultraviolet; 13nm) and have employed photoresist resins having a low transmittance to the short wavelengths, resulting in poor quality patterns. For example, a photoresist resin which has been used with i-line (365nm) and KrF (248nm) light sources contains aromatic compounds, which have a relatively high absorbance of 193 nm wavelength light. Photoresists comprising acrylic or alicyclic resins which do not contain aromatic compounds have also been synthesized and used, unfortunately, these resins also have a relatively high absorbance of 193 nm wavelength light.

Use of conventional chemically amplified photoresist resins having a low transmittance is undesirable because the low transmittance results in more light reaching the upper portion of the photoresist than the bottom portion, which results in higher acid concentration in the upper portion of the photoresist than in the bottom portion of the photoresist, which can result in a bulk slope profile pattern. See Figure 1b. This is contrasted to a pattern formed when the photoresist resin has a relatively low light absorbance. In this case, the amount of light reaching the upper and bottom portions of the photoresist is nearly identical, thus forming a desired vertical pattern. See Figure 1a.

In order to overcome the above disadvantages, efforts have been directed at synthesizing resins having a low light absorbance. Unfortunately, these attempts have proven unsuccessful in particular for light wavelengths of 157 nm (F_2) and 13 nm (EUV).

The present inventor found that the vertical pattern could be obtained when an amine compound is added to the over-coating material for photoresist even when a photoresist resin has a relatively high absorbance to light used in pattern formation, and

accomplished the present invention.

SUMMARY OF THE INVENTION

An object of the present invention is to provide processes for forming a vertical photoresist pattern, even when a photoresist resin has a relatively high absorbance to light used in pattern formation.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides an over-coating composition comprising a basic compound, which achieves the above-stated objectives. The basic compound in the over-coating composition diffuses or penetrates into the photoresist film layer, and neutralizes at least a portion of the acids in the upper portion of the photoresist film, thereby providing vertical patterns.

The present invention is described in more detail, hereinafter.

The present invention provides a process for forming a vertical photoresist pattern, even when a photoresist resin has a relatively high absorbance to light used in pattern formation. In order to provide the above process, the present invention provides an over-coating composition comprising a basic compound such as amine.

In one particular aspect, the present invention provides an over-coating composition comprising (i) an over-coating resin, (ii) a solvent, and (iii) a material which functions as strong or weak base.

Amine compound is preferably used as a material which functions as strong or weak base. Exemplary amine compounds are amino acid such as L-proline or water-soluble amine such as tetramethylammonium hydroxide (TMAH).

Further to the amine compound, amide compounds, urethane compounds

and urea compound can be used as a material which functions as strong or weak base.

The over-coating resin of the present invention can be any of conventional resin used for over-coating material. A particularly useful over-coating resin includes poly(acrylic acid / methyl acrylate).

Preferably, the solvent in the over-coating composition is distilled water.

It is believed for a photoresist resin having a low transmittance, more acid is generated in the upper portion of the photoresist film than the bottom portion (see Figure 1b). It is believed that the basic compound in the over-coating composition diffuses or penetrates into the photoresist film layer, and neutralizes at least a portion of the acids in the upper portion of the photoresist film, thereby providing a more uniform acid concentration throughout the photoresist film depth. For example, as the basic compound penetrates into the photoresist film, initially a large amount of basic compound is present in the upper portion of the photoresist film relative to the bottom portion of the photoresist film. Some of these basic compounds are neutralized by the acids that are generated by photolysis, thus there is a gradual decrease in the amount of basic compound diffusing further down towards the lower portion of the photoresist film. This results in a basic compound gradient along the depth of the photoresist film preventing or reducing the formation of a sloped photoresist pattern caused by a high light absorbance by the photoresist resin.

The present invention also provides a process for forming a photoresist pattern comprising the steps of:

(a) coating a photoresist composition on a substrate to form a photoresist film;

(b) coating the over-coating composition of the photoresist film to produce an over-coated substrate;

(c) exposing the over-coated substrate to light using a light source; and

(d) developing the light exposed over-coated substrate.

The photoresist composition can comprise any currently known chemically amplified photoresist resin, including poly(tert-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / 2-hydroxyethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / bicyclo[2.2.1]hept-5-ene-2-carboxylic acid / maleic anhydride).

The process for producing the photoresist pattern can also comprise baking step(s) before and/or after exposing the over-coated substrate light. The baking step is typically performed at temperature of from about 10 to about 200 °C.

Exemplary light sources which are useful for forming a photoresist pattern include ArF (193nm), KrF (248nm), F_2 (157nm), EUV (13nm), E-beam, X-ray and ion beam.

In another embodiment, the present invention also provides a semiconductor element that is manufactured using the over-coating composition described above.

The present invention will now be described in more detail by referring to the examples below, which are not intend to be limiting.

Invention Example 1. Measurement of Absorbance

DHA1001 (a photoresist composition manufactured by Dong-jin Semichem Inc.) comprising poly(tert-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / 2-hydroxyethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / bicyclo[2.2.1]hept-5-ene-2-carboxylic acid / maleic anhydride) as a photoresist resin was coated on a quartz-wafer, baked at 150 °C for 90 seconds, and cooled to 23 °C (photoresist thickness: about 1μm). Here, transmittance of the photoresist measured by JASCO VUV 200 spectrometer was 45%.

Comparative Example 1

At an environmental amine concentration of 1 ppb, the photoresist composition used in Invention Example 1 was coated on the wafer at a thickness of about 0.4 μm, baked at 150 °C for 90 seconds, and cooled to 23 °C.

Thereafter, the coated photoresist was exposed to light using an ArF exposer, baked at 140 °C for 90 seconds, and developed in 2.38 wt% TMAH solution to obtain a 140 nm L/S pattern. As shown in Figure 2, the photoresist pattern was severely sloped due to the low transmittance of the photoresist composition.

Comparative Example 2

The procedure of Comparative Example 1 was repeated, except the environmental amine concentration was 5 ppb instead of 1 ppb. A vertical pattern shown in Figure 3 was obtained.

Comparative Example 3

The procedure of Comparative Example 1 was repeated, except the environmental amine concentration was 40 ppb instead of 1 ppb. A photoresist pattern having a rounded upper portion shown in Figure 4 was obtained.

As shown in the Comparative Examples 1 to 3, when the concentration of environmental amine is low, a relatively severely sloped photoresist pattern was obtained due to a low transmittance of the photoresist (see Figure 2). As described above with reference to Figure 1b, it is believed that this sloping photoresist pattern is due to the fact that the amount of light reaching the upper portion of the photoresist film is greater than the amount of light reaching the bottom portion of the photoresist film, which results in a

higher amount acids generated in the upper portion of the photoresist film. But as can be seen in Figure 3, a vertical photoresist pattern is formed when the concentration of environmental amine is increased from 1 ppb to 5 ppb. It is believed that this is because the environmental amine come in contact with and penetrates into the photoresist and neutralizes the acid in the upper portion of the photoresist film, while only a small amount of the environmental amine compound penetrates into the bottom portion of the photoresist film. Thus, when the amount of environmental amine present is high, the acid concentration gradient along the depth of the photoresist film, which is produced by a photolysis of photoresist composition having a high absorbance, is minimized by a similar environmental amine compound gradient along the depth of the photoresist film. This results in a vertical photoresist pattern as shown in Figure 3.

However, when the concentration of the environmental amine compound is 40 ppb or more, the amount of environmental amine compound is significantly higher than the amount of acid that is typically generated during the photolysis resulting in a photoresist pattern having a swollen upper portion as shown in Figure 4.

At the environmental amine concentration of 5 ppb, a high quality photoresist pattern was obtained using a low transmittance photoresist resin. Unfortunately, the environmental amine concentration can not be maintained constantly at 5 ppb throughout a semiconductor device fabrication process. Typically, the environmental amine concentration varies continuously during an actual semiconductor device fabrication process.

<u>Preparation Example. Synthesis of Over-coating Resin</u>

9g of acrylic acid, 1g of methyl acrylate, 50g of isobutyl methyl ketone, 50g of propylene glycol methyl ether acetate and 0.3g of AIBN were combined and heated to

about 67 °C for 3 hours under an inert atmosphere (e.g., nitrogen gas). The precipitated polymer was washed with ethyl ether and vacuum dried to obtain pure poly(acrylic acid / methyl acrylate) resin (weight average molecular weight: 7200, yield: 54%).

Comparative Example 4. Preparation of Over-coating Composition

To 200g of distilled water was added 5g of poly(acrylic acid / methyl acrylate) resin prepared in the Preparation Example. The resulting solution was filtered through 0.20μm-filter to produce an over-coating composition.

Invention Example 2. Synthesis of Over-coating Composition Containing Basic compound

To 200g of distilled water was added 0.16g of L-proline and 5g of poly(acrylic acid / methyl acrylate). The resulting solution was filtered through 0.20μm-filter to produce the over-coating composition of the present invention.

Comparative Example 5

DHA1001 photoresist composition used in Invention Example 1 was coated on a wafer, baked at 110 °C for 90 seconds, and cooled to 23 °C in an environmental amine concentration of 20 ppb. The over-coating composition of Comparative Example 4 which does not contain L-proline was coated on the photoresist film, baked at 60°C for 60 seconds, and cooled. After baking, the wafer was exposed to light using an ArF laser exposer, and then post-baked at 110°C for 90 seconds. When the post-baking was completed, it was developed in 2.38wt% aqueous TMAH solution to obtain a 140nm L/S pattern. As shown in Figure 5, the photoresist pattern was sloped similar to those shown in Figure 1b and Figure 2. When the over-coating composition was not used (similar to Comparative Example 2) the vertical pattern was formed at the environmental amine

concentration of 5 ppb. However, at the environmental amine concentration of 20 ppb, a relatively severely sloped photoresist pattern was formed even though an over-coating composition was used (see Figure 5). It is believed that this sloping photoresist pattern is due to (i) the environmental amine concentration being too high, (ii) the over-coating composition having an insufficient amount of the basic compound to neutralize the acids in upper portion of the photoresist film, and/or (iii) the over-coating composition blocking the environmental amines from penetrating into the photoresist film thereby preventing neutralization of at least a portion of the acids in upper portion of the photoresist film.

Invention Example 3

DHA1001 photoresist composition was coated on a wafer, baked at 110°C for 90 seconds, and cooled to 23°C in an environmental amine concentration of 20ppb. Thereafter, the over-coating composition of Invention Example 2 containing L-proline was over-coated on the photoresist film, baked at 60°C for 60 seconds, and cooled. After baking, the wafer was exposed to light using an ArF laser exposer, and then post-baked at 110°C for 90 seconds. When the post-baking was completed, it was developed in 2.38wt% aqueous TMAH solution to obtain a 140nm L/S pattern (see Figure 6).

The pattern profile shown in Figure 6 is vertical similar to that shown in Figure 1a and Figure 3. It is believed that L-proline in the over-coating composition penetrates into the photoresist film layer and neutralizes at least a portion of a large amount of acids that are generated in the upper portion of the photoresist, thereby preventing or significantly reducing the formation of a sloped photoresist pattern.

EFFECT OF THE INVENTION

As shown above, when the over-coating composition of the present

invention is used, it is believed that the basic compound in the over-coating composition penetrates into the photoresist film layer, thereby providing an amine gradient within the photoresist film. Accordingly, a relatively large amount of acid on the upper portion of the photoresist film is neutralized resulting in a vertical photoresist pattern even when the photoresist resin has a high light absorbance.

What is claimed is:

1. An over-coating composition for coating a photoresist composition, comprising (i) an over-coating resin, (ii) a solvent, and (iii) a material which functions as strong or weak base.

2. The over-coating composition according to claim 1, wherein said material which functions as strong or weak base is selected from the group consisting of an amine compound; an amide compound; an urethane compound; and an urea compound.

3. The over-coating composition according to claim 1, wherein said amine is L-proline or tetramethylammonium hydroxide (TMAH).

4. The over-coating composition according to claim 1, wherein said over-coating resin is poly(acrylic acid / methyl acrylate), and said solvent is distilled water.

5. A process for forming a photoresist pattern, comprising the steps of:

(a) coating a photoresist composition on a substrate to form a photoresist film;

(b) coating an over-coating composition of claim 1 on the upper portion of said photoresist film to form a over-coating;

(c) exposing said over-coated substrate to light using a light source; and

(d) developing said exposed over-coated substrate.

6. The process according to claim 5, wherein said photoresist composition comprises a commonly used photoresist resin.

7. The process according to claim 6, wherein said photoresist resin is poly(tert-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / 2-hydroxyethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / bicyclo[2.2.1]hept-5-ene-2-carboxylic acid / maleic anhydride).

8. The process according to claim 5 further comprising a baking step before and/or after said exposure step (c).

9. The process according to claim 8, wherein said baking step is performed at a temperature range of from 10 to 200°C.

10. The process according to claim 5, wherein said light source is ArF (193nm), KrF (248nm), F_2 (157nm), EUV (13nm), E-beam, X-ray or ion beam.

11. A semiconductor element manufactured by the process according to claim 5.

ABSTRACT

The present invention provides an over-coating composition comprising a basic compound for coating a photoresist composition. When the over-coating composition of the present invention is used, it is believed that the basic compound in the over-coating composition penetrates into the photoresist film layer, thereby providing an amine gradient within the photoresist film. Accordingly, a relatively large amount of acid on the upper portion of the photoresist film is neutralized resulting in a vertical photoresist pattern even when the photoresist resin has a high light absorbance.